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(54) **Ene-yne unsaturated compounds as accelerators for hydrosilation**

(57) A hydrosilation process where a silicon hydride is reacted with an unsaturated reactant in the presence of a platinum catalyst and an accelerator selected from ene-yne unsaturated compounds. The accelerators are

especially useful for facilitating the hydrosilation of unsaturated reactants where the unsaturation is in the internal portion of the reactant's structure, for example, as in cyclopentene or cyclohexene.

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Description

The present invention is a hydrosilation process where a silicon hydride is reacted with an unsaturated reactant in the presence of a platinum catalyst and an accelerator selected from ene-yne unsaturated compounds. The accelerators are especially useful for facilitating the hydrosilation of unsaturated reactants where the unsaturation is in the internal portion of the reactant's structure, for example, as in cyclopentene or cyclohexene. These accelerators are believed to be effective in the presence or absence of oxygen.

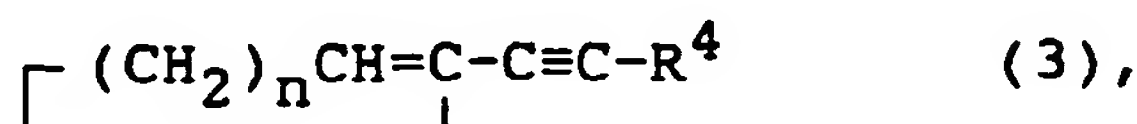
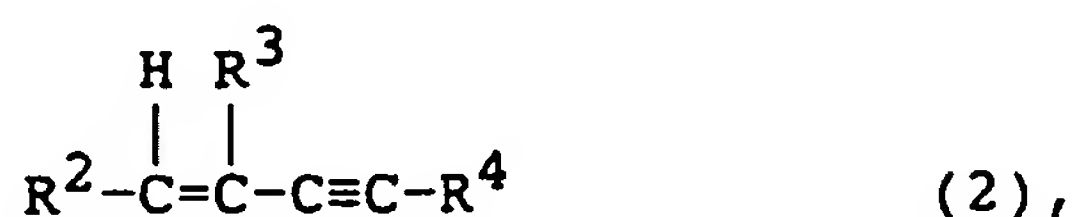
It is known in the art to produce organosilicon compounds by reacting a silicon hydride containing compound with an unsaturated organic compound in the presence of a catalyst. This reaction is typically referred to as hydrosilation or hydrosilylation. Typically, the catalyst is platinum metal on a support, a platinum compound usually in a solvent or a platinum complex.

In US Patent 2,823,218, a method for the production of organosilicon compounds by reacting an Si-H with a compound containing aliphatic carbon atoms linked by multiple bonds in the presence of chloroplatinic acid is taught. US Patent 3,220,972 discloses a similar process, however, the catalyst is a reaction product of chloroplatinic acid.

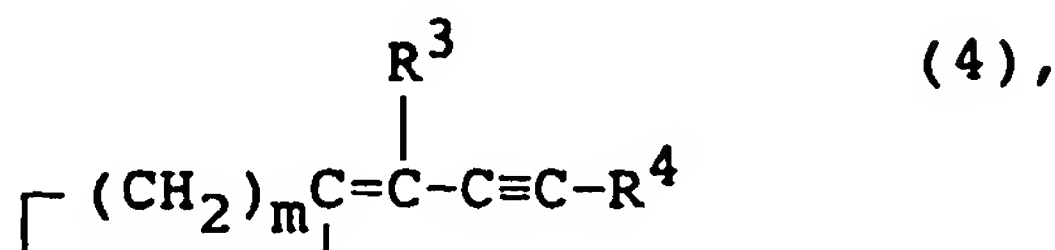
One of the major problems in the art with hydrosilation reactions is the deactivation of the catalyst prior to reaction completion. One method for catalyst reactivation has been to expose the reaction mixture to oxygen. For example, US Patent 4,578,497 claims the use of an oxygenated platinum-containing catalyst for use in hydrosilating alkylsilanes. US Patent 5,359,111 provides a method for controlling hydrosilation reaction mixtures by controlling the solution concentration of oxygen in the reaction mixture, relative to the platinum present in the reaction mixture.

In addition to the deactivation problem of the platinum catalyst, hydrosilation processes taught in the art are not particularly effective in hydrosilating internal unsaturated bonds in organic molecules. We have unexpectedly found that ene-yne unsaturated compounds, ene-yne unsaturated alcohols and silylated ene-yne unsaturated alcohols can also act as accelerators for platinum catalyzed hydrosilation processes. The accelerators are believed to improve yield of the process in the presence or absence of oxygen and they are particularly effective in facilitating the hydrosilation of internal unsaturated bonds of organic molecules.

The present invention is a hydrosilation process where a silicon hydride is reacted with an unsaturated reactant in the presence of a platinum catalyst and a novel accelerator. The hydrosilation process comprises contacting (A) a silicon hydride described by formula $R^1_a H_b SiX_{4-a-b}$ (1) where each R^1 is independently selected from a group consisting of alkyls comprising one to 20 carbon atoms, cycloalkyls comprising four to 12 carbon atoms and aryls; each X is independently selected from halogen atom or organooxy radicals described by formula $-OR^1$, where R^1 is as previously described, $a=0$ to 3, $b=1$ to 3 and $a+b=1$ to 4; and (B) an unsaturated reactant selected from a group consisting of (i) substituted or unsubstituted unsaturated organic compounds, (ii) silicon compounds comprising substituted or unsubstituted unsaturated organic substituents, and (iii) mixtures of (i) and (ii); in the presence of a platinum catalyst selected from platinum compounds or platinum complexes and an accelerator selected from a group consisting of ene-yne unsaturated compounds described by formulas



and



where R^2 is selected from hydrogen atom or hydrocarbon radicals comprising one to 12 carbon atoms, R^3 is selected from hydrogen atom or hydrocarbon radicals comprising one to six carbon atoms, R^4 is selected from a group consisting

of hydrogen atom, hydrocarbon radicals comprising one to six carbon atoms and triorganosilyl radicals described by formula $-\text{SiR}^5_3$, where each R^5 is an independently selected hydrocarbon radical comprising one to six carbon atoms, $n=3$ to 5 and $m=4$ to 6.

The contacting of the silicon hydride with the unsaturated reactant is effected in standard type reactors for conducting hydrosilation processes. The contact and reaction may be run as a continuous, semi-continuous or batch reaction.

Silicon hydrides useful in the present process are described by formula (1), where each R^1 is independently selected from a group consisting of alkyls comprising one to 20 carbon atoms, cycloalkyls comprising four to 12 carbon atoms and aryls; $a=0$ to 3, $b=1$ to 3 and $a+b=1$ to 4. R^1 is a substituted or unsubstituted alkyl, cycloalkyl or aryl as previously described.

In formula (1), it is preferred that each R^1 be independently selected from alkyls comprising one to six carbon atoms. Even more preferred is when each R^1 is methyl.

In formula 1, each X is independently selected from halogen atom or organooxy radicals described by formula $-\text{OR}^1$, where R^1 is as previously described. Preferred is when X is chlorine.

Examples of silicon hydrides described by formula (1) which are useful in our claimed process include trimethylsilane, dimethylsilane, triethylsilane, dichlorosilane, trichlorosilane, methyldichlorosilane, dimethylchlorosilane, ethyldichlorosilane, cyclopentylidichlorosilane, methylphenylchlorosilane, (3,3,3-trifluoropropyl)dichlorosilane and methylmethoxychlorosilane. A preferred silicon hydride described by formula (1) is selected from methyldichlorosilane or dichlorosilane.

The silicon hydride is contacted with an unsaturated reactant selected from a group consisting of (i) substituted or unsubstituted unsaturated organic compounds, (ii) silicon compounds comprising substituted or unsubstituted unsaturated organic substituents, and (iii) mixtures of (i) and (ii). For this invention, "unsaturated" means that the compound contains at least one carbon-carbon double bond.

More specific examples of the unsaturated reactants useful in our process include unsubstituted cycloalkene compounds comprising at least four carbon atoms, substituted cycloalkene compounds comprising at least four carbon atoms, linear alkene compounds comprising two to 30 carbon atoms, branched alkene compounds comprising four to 30 carbon atoms and mixtures of two or more of any of the above.

The substituted and unsubstituted cycloalkene compounds useful in the present process are those containing one or more unsaturated carbon-carbon bonds in the ring. The unsubstituted cycloalkene compounds may be, for example, cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclopentadiene, 1,3-cyclohexadiene and 1,3,5-cycloheptatriene. Substituted unsaturated compounds useful in this invention are, for example, 3-methylcyclopentene, 3-chlorocyclobutene, 4-phenylcyclohexene and 3-methylcyclopentadiene. The preferred cycloalkene compounds are cyclohexene and cyclopentene, with cyclohexene being the most preferred.

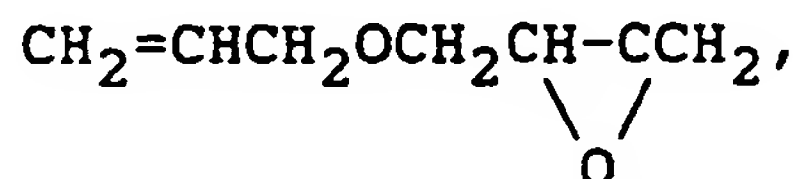
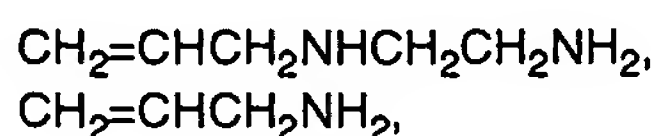
Other unsaturated organic compounds useful in our process are linear and branched alkenyl compounds including, for example, compounds with terminal unsaturation such as 1-hexene and 1,5-hexadiene, compounds with internal unsaturation such as trans-2-hexene and unsaturated aryl containing compounds such as styrene and α -methylstyrene.

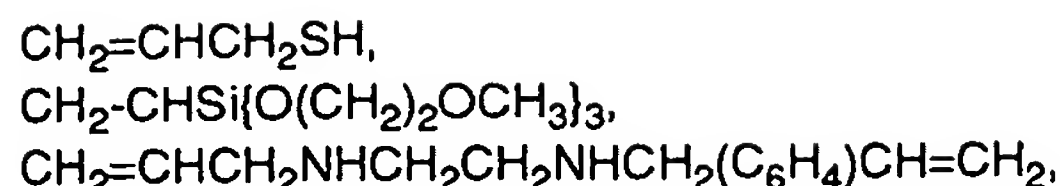
The unsaturated reactants may also comprise halogen, oxygen in the form of acids, anhydrides, alcohols, esters, ethers and nitrogen. Mixtures of two or more of the above described unsaturated organic compounds may also be used in the present process.

The unsaturated organic compounds comprising halogen may include, for example, vinyl chloride, allyl chloride, allyl bromide, allyl iodide, methallyl chloride, trichloroethylene, tetrachloroethylene, tetrafluoroethylene, chloroprene, vinylidene chloride and dichlorostyrene.

Suitable unsaturated organic compounds comprising oxygen include, for example, ethers such as allyl and vinyl ethers; alcohols such as allyl alcohol (vinyl carbinol), methylvinylcarbinol and ethynyldimethyl-carbinol; acids such as acrylic, methacrylic, vinylacetic, oleic, sorbic and linolenic; and esters such as vinyl acetate, allyl acetate, butenyl acetate, allyl stearate, methylacrylate, ethylcrotonate, diallyl succinate and diallyl phthalate. Suitable nitrogen containing unsaturated organic compounds include, for example, indigo, indole, acrylonitrile and allyl cyanide.

Specifically included within the definition of unsaturated organic compounds are those substituted by organofunctional moieties such as $\text{CH}_2=\text{CHCH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$,





5 and similar compounds.

The unsaturated organic compound can also be a silicon compound comprising substituted and unsubstituted organic substituents as described by, for example, formulas $(\text{CH}_2=\text{CH}(\text{CH}_2)_g)_h\text{R}^1\text{Si}(\text{OR}^1)_{4-h-i}$ and $(\text{CH}_2=\text{CH}(\text{CH}_2)_g)_h\text{R}^1\text{SiCl}_{4-h-i}$, where R is as previously described, $g=0$ to 12, $h=1$ to 3, $i=0$ to 3 and $h+i=1$ to 4.

10 Prior to contact of the silicon hydride with the unsaturated reactant, it may be preferable to treat or purify the unsaturated reactant. Such methods for treating or purifying the unsaturated reactants are those known in the art and include distillation or treatment with an adsorbent such as activated alumina or molecular sieves.

The relative amounts of silicon hydride and unsaturated reactant used in the present process can be varied within wide limits. Although one unsaturated carbon-carbon linkage per silicon bonded hydrogen atom is stoichiometric, there is no requirement that the process be run under stoichiometric conditions. Generally, it is preferred that the process
15 be run with a stoichiometric excess of silicon hydride. Preferred is when the process is run with 0.1 to ten percent stoichiometric excess of silicon hydride. However, for safety reasons, it may be preferred to run the process with an excess of unsaturated reactant, for example, when the silicon hydride is dichlorosilane.

The silicon hydride and unsaturated reactant are contacted in the presence of a platinum catalyst selected from platinum compounds and platinum complexes. Any platinum containing material which effects the reaction between
20 the silicon hydride and an unsaturated carbon-carbon bond of the unsaturated organic compound is useful in the present invention. Examples of useful platinum catalysts are described, for example, in US Patents 4,578,497; 3,220,972 and 2,823,218.

The platinum catalyst can be, for example, chloroplatinic acid, chloroplatinic acid hexahydrate, Karstedt's catalyst (i.e., a complex of chloroplatinic acid with sym-divinyldimethylsiloxane), dichloro-bis(triphenylphosphine)platinum (II), cis-dichloro-bis(acetonitrile)platinum(II), dicarbonyldichloroplatinum(II), platinum chloride and platinum oxide.
25

A preferred platinum catalyst is selected from the group consisting of chloroplatinic acid, chloroplatinic acid hexahydrate and platinum vinylsiloxane complexes such as a neutralized complex of chloroplatinic acid or platinum dichloride with sym-divinyldimethylsiloxane.

Generally, those concentrations of platinum catalyst which provide at least one mole of platinum per billion moles
30 of unsaturated carbon-carbon bonds added to the process by the unsaturated reactant are useful in the present process. Concentrations of platinum catalyst providing as high as one mole of platinum per one thousand moles of unsaturated carbon-carbon bonds added to the process by the unsaturated reactant are also useful.

The platinum catalyst may be dissolved in a solvent for ease of handling and to facilitate measuring of the small amounts typically needed. Suitable solvents include, for example, non-polar hydrocarbon solvents such as benzene,
35 toluene and xylene and polar solvents such as alcohols, ketones, glycols and esters.

The present process is carried out in the presence of an accelerator selected from ene-yne unsaturated compounds as described by formulas (2), (3) and (4) herein. In formula (2), R^2 is selected from hydrogen atom or hydrocarbon radicals comprising one to 12 carbon atoms. R^2 can be saturated or unsaturated and substituted or unsubstituted. R^2
40 can be substituted with, for example, hydroxy, siloxy or a halogen. The preferred substitution in R^2 is hydroxy. In addition to hydrogen, R^2 can be, for example, alkyls such as methyl, ethyl, tert-butyl, pentyl and decyl; substituted alkyls such as hydroxymethyl, 2-hydroxyethyl and 3-hydroxypentyl; alkenyls such as vinyl, allyl and hexenyl; aryls such as phenyl; and siloxyalkyls such as chloromethylhydrosiloxymethyl or chlorocyclopentylmethylsiloxyethyl.

In formulas (2) and (4), R^3 is selected from hydrogen atom or hydrocarbon radicals comprising one to six carbon atoms. Preferred is when R^3 is selected from hydrogen atom or alkyls comprising one to six carbon atoms. Most
45 preferred is when R^3 is selected from hydrogen and methyl.

In the formulas (2), (3) and (4), R^4 is selected from a group consisting of hydrogen atom, hydrocarbon radicals comprising one to six carbon atoms and triorganosilyl radicals described by formula $-\text{SiR}^5_3$, where each R^5 is an independently selected hydrocarbon radical comprising one to six carbon atoms. Preferred is when R^4 is selected from
50 a group consisting of hydrogen atom, alkyls comprising one to six carbon atoms, hydroxy substituted alkyls comprising one to six carbon atoms, siloxy substituted alkyls where the alkyl comprises one to six carbon atoms and triorganosilyl radicals described by the formula $-\text{SiR}^5_3$, where each R^5 is an independently selected alkyl comprising one to six carbon atoms. Preferred is where R^5 is methyl. Most preferred is when R^4 is hydrogen.

In formula (3), n can have a value of 3, 4 or 5. Preferred is when n has a value of 3 or 4. In formula (4), m can have a value of 4, 5 or 6. Preferred is when m as a value of 4 or 5.

55 Examples of ene-yne unsaturated compounds which are useful in the present process include: 2-methyl-1-buten-3-yne, 3,5-dimethyl-3-hexen-1-yne, 2-penten-4-yn-1-ol, 3-methyl-2-penten-4-yn-1-ol, 3-nonen-1-yne, 3-penten-1-yne, 2-methyl-4-trimethylsilyl-1-buten-3-yne, 4-methyl-4-penten-2-yn-1-ol, 2,5-dimethyl-5-hexen-3-yn-2-ol, 3,6-dimethyl-6-hepten-4-yn-3-ol, 6-methyl-6-hepten-4-yn-3-ol, 1-(2',6',6'-trimethylcyclohex-1'-enyl)but-1-ene-3-yne, 1-ethynylcy-

cyclohexene, 1-ethynyl-1-cyclopentene, 1-cyclohexenylpropyne, (1-cyclohexen-1-ylethynyl)trimethylsilane and propynylidenecyclohexane.

A preferred accelerator for use in our process is selected from the group consisting of 3,5-dimethyl-3-hexen-1-yne, 3-methyl-2-penten-4-yn-1-ol, 1-ethynylcyclohexene, 1-chloromethylhydridosiloxy-3-methyl-2-penten-4-yne and 1-chlorocyclopentylmethylsiloxy-3-methyl-2-penten-4-yne.

An effective concentration of the accelerator is added to the present process, where an effective concentration is one that facilitates initiation of the reaction between the silicon hydride and the unsaturated organic compound, accelerates the rate of the reaction and/or reduces loss of reactivity of the catalyst in the process. A useful effective concentration of the accelerator is generally within a range of 0.01 to 20 weight percent of the weight of the unsaturated reactant. Preferred is when the accelerator is 0.1 to ten weight percent of the unsaturated reactant. The accelerator may be added to the process as a pre-mix with the platinum catalyst or separately.

The temperature at which the present process is conducted can generally be within a range of -10°C. to 220°C. It is preferred to conduct our process at a temperature of 15°C. to 170°C. The most preferred temperature for the process is within a range of 30°C. to 150°C.

Example 1

The ability of ene-yne unsaturated compounds to accelerate the reaction of methyldichlorosilane with cyclohexene in the presence of a platinum catalyst was evaluated. A stock mixture was prepared in an argon purged and blanketed bottle. The stock mixture comprised four molar percent excess of methyldichlorosilane in cyclohexene which had been treated with 13X molecular sieves. Then 6×10^{-5} moles of platinum, as a platinum divinylsiloxane complex, per mole of cyclohexene was added to the stock mixture. Aliquots of the catalyzed stock solution were then transferred to argon-purged glass tubes and ene-yne unsaturated compounds as described in Table 1 were added to the tubes at a concentration of one weight percent of the cyclohexene. The tubes were heat sealed under argon purge and heated at 80°C. for three hours. At the end of three hours, the tubes were cooled and the contents analyzed by gas chromatography using a thermal conductivity detector (GC-TC). The results of this analysis are reported in Table 1 as the normalized area percent of (cyclohexyl)methyldichlorosilane ($\text{MeC}_6\text{H}_{11}\text{SiCl}_2$) under the GC-TC trace minus the area of the cyclohexene as 100 percent.

TABLE 1

| Ene-yne Unsaturated Compounds as Accelerators For Platinum Catalyzed Addition of MeHSiCl_2 to Cyclohexene | |
|--|---|
| Type Accelerator | Area% $\text{Me}(\text{C}_6\text{H}_{11})\text{SiCl}_2$ |
| None | 22.1 |
| 3,5-Dimethyl-3-hexen-1-yne | 80.7 |
| 3-Methyl-2-penten-4-yn-1-ol | 95.9 |
| 1-Ethynylcyclohexene | 71.5 |

Example 2

The ability of 1-ethynylcyclohexene to accelerate the reaction of dichlorosilane with cyclopentene in the presence of a platinum catalyst was evaluated.

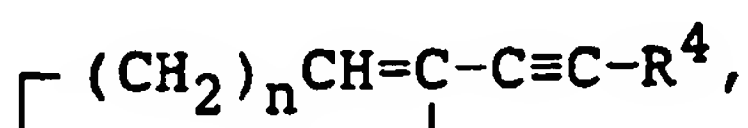
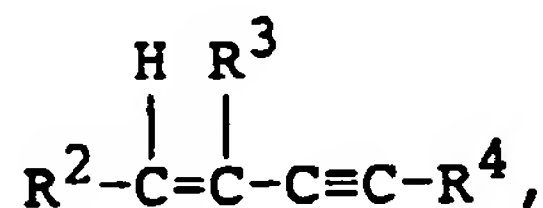
A stock mixture comprising 14.2 weight percent dichlorosilane in cyclopentene was prepared in an argon purged and blanketed bottle. Aliquots of the mixture were transferred to argon purged glass tubes containing a platinum divinylsiloxane complex providing 7×10^{-4} moles of platinum per mole of dichlorosilane. Next, one weight percent of 1-ethynylcyclohexene based on the total mass was added to the tubes. The tubes were heat sealed under an argon blanket and heated at 120°C. for the times given in Table 2. After heating, the tubes were cooled and the contents analyzed by GC-TC. The results of the analysis are reported in Table 2 as the normalized area percent of cyclopentyl-dichlorosilane (CpHSiCl_2) and dicyclopentyl-dichlorosilane (Cp_2SiCl_2) under the GC-TC trace minus the area of the cyclopentene as 100 percent.

TABLE 2

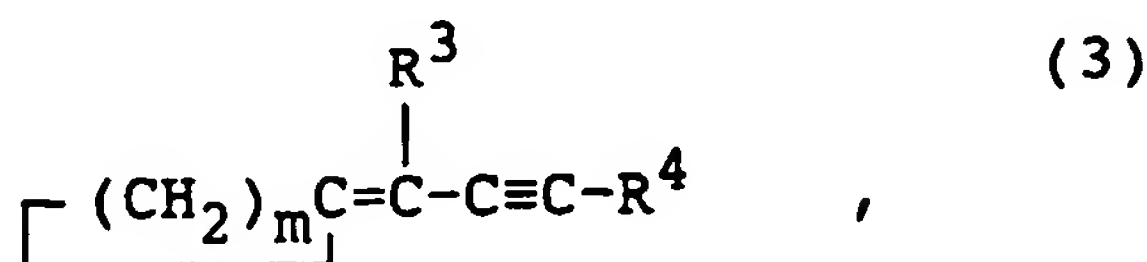
| 1-Ethynylcyclohexene as Accelerator For Platinum Catalyzed Addition of Dichlorosilane to Cyclopentene | | | |
|---|----------|--------------------------|----------------------------------|
| Accelerator | Time (h) | Area% CpHSiCl_2 | Area% Cp_2SiCl_2 |
| None | 1.5 | 76.7 | 0.0 |
| 1-Ethynylcyclohexene | 1.0 | 62.3 | 4.3 |

Claims

1. A hydrosilation process comprising contacting (A) a silicon hydride described by formula $R^1_a H_b SiX_{4-a-b}$, where each R^1 is independently selected from a group consisting of alkyls comprising one to 20 carbon atoms, cycloalkyls comprising four to 12 carbon atoms and aryls; each X is independently selected from halogen atom or organooxy radicals described by formula $-OR^1$, where R^1 is as previously described, $a=0$ to 3, $b=1$ to 3 and $a+b=1$ to 4; and (B) an unsaturated reactant selected from a group consisting of (i) substituted or unsubstituted unsaturated organic compounds, (ii) silicon compounds comprising substituted or unsubstituted unsaturated organic substituents, and (iii) mixtures of (i) and (ii); in the presence of a platinum catalyst selected from platinum compounds or platinum complexes and an accelerator selected from a group consisting of ene-yne unsaturated compounds described by formulas



and



where R^2 is selected from hydrogen atom or hydrocarbon radicals comprising one to 12 carbon atoms, R^3 is selected from hydrogen atom or hydrocarbon radicals comprising one to six carbon atoms, R^4 is selected from a group consisting of hydrogen atom, hydrocarbon radicals comprising one to six carbon atoms and triorganosilyl radicals described by formula $-SiR^5_3$, where each R^5 is an independently selected hydrocarbon radical comprising one to six carbon atoms, $n=3$ to 5 and $m=4$ to 6.

2. A process according to claim 1 where the silicon hydride (A) is selected from methyldichlorosilane or dichlorosilane.
3. A process according to claim 1 or 2 where the unsaturated reactant (B) is selected from cyclohexene or cyclopentene.
4. A process according to any of claims 1 to 3 where the unsaturated reactant (B) is contacted with a stoichiometric excess of the silicon hydride (A).
5. A process according to any of claims 1 to 4 where R^2 is a hydrocarbon radical substituted with hydroxy.
6. A process according to any of claims 1 to 5 where R^3 is selected from hydrogen atom or alkyls comprising one to six carbon atoms.
7. A process according to any of claims 1 to 6 where R^4 is selected from a group consisting of hydrogen atom, alkyls comprising one to six carbon atoms, hydroxy substituted alkyls comprising one to six carbon atoms, siloxy substituted alkyls where the alkyl comprises one to six carbon atoms and triorganosilyl radicals described by formula $-SiR^5_3$ where each R^5 is an independently selected alkyl comprising one to six carbon atoms.
8. A process according to any of claims 1 to 7 where the accelerator is selected from a group consisting of 3,5-dimethyl-3-hexen-1-yne, 3-methyl-2-penten-4-yn-1-ol, 1-ethynylcyclohexene, 1-chloromethylhydrosiloxy-3-methyl-2-penten-4-yne and 1-chlorocyclopentylmethylsiloxy-3-methyl-2-penten-4-yne.

9. A process according to any of claims 1 to 8 where concentration of the accelerator is within a range of 0.01 to 20 weight percent of the weight of the unsaturated reactant.
10. A process according to any of claims 1 to 9 where the silicon hydride is contacted with the unsaturated reactant at a temperature within a range of about -10°C. to 220°C.
11. A process according to any of claims 1 to 10 where the silicon hydride is methyldichlorosilane, the unsaturated reactant is cyclohexene, the platinum catalyst is a platinum vinylsiloxane complex and the accelerator is selected from a group consisting of 3,5-dimethyl-3-hexen-1-yne, 3-methyl-2-penten-4-yn-1-ol and 1-ethynylcyclohexene.
12. A process according to any of claims 1 to 10 where the silicon hydride is dichlorosilane, the unsaturated reactant is cyclopentene, the platinum catalyst is a platinum vinylsiloxane complex and the accelerator is 1-ethynylcyclohexene.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 4405

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| A | EP 0 460 589 A (SHIN-ETSU CHEMICAL CO., LTD.) * the whole document * | 1-12 | C07F7/14 |
| A | EP 0 510 957 A (GENERAL ELECTRIC COMPANY) * the whole document * | 1-12 | |
| A | EP 0 091 291 A (TORAY SILICONE CO., LTD., JAPAN) | 1-12 | |
| A | CHEMICAL ABSTRACTS, vol. 105, no. 26, 29 December 1986 Columbus, Ohio, US; abstract no. 228651, SASAKI, SHOSAKU ET AL: "Siloxane release coatings" XP002035615 * abstract * & JP 61 162 561 A (TORAY SILICONE CO., LTD., JAPAN) | 1-12 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| | | | C07F |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 18 July 1997 | Examiner Rinkel, L |
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